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(54) [Title of the invention]

Electro-photographic Photoreceptor.

(57) [Summary] (There exists a correction)

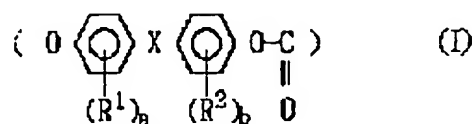
[Aim]

To offer an electro-photographic photoreceptor that has excellent practical use, with no whitening (gelation) of coating liquid taking place at the time of manufacture of electro-photographic photoreceptor, and that maintains excellent mechanical strength such as printing resistance for a long period and has excellent electro-photography property.

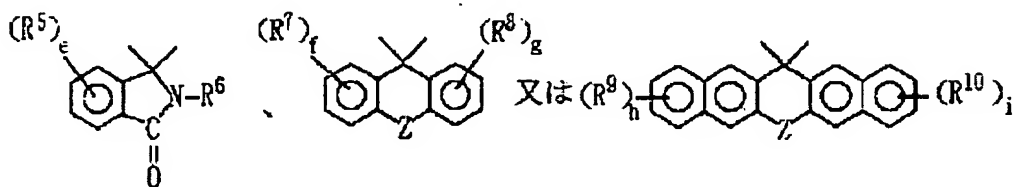
[Composition]

In the electro-photographic photoreceptor consisting of a photosensitive layer formed on electro-conductive baseboard, a polycarbonate possessing the repetitive units shown by the formula (I) given below is used as the binder

resin for the photosensitive layer mentioned above.



[Wherein,  $\text{R}^1$  and  $\text{R}^2$  independently show halogen atom etc.,  
a and b are integers from 0 ~ 4 and X is the radical shown  
by the formula given below.



(Wherein,  $\text{R}^5$ ,  $\text{R}^7 \sim \text{R}^{10}$  mean the same as  $\text{R}^1$ ,  $\text{R}^6$  shows alkyl  
radical having 1 ~ 12 carbon atoms, Z is a single bond or  
- O -, e, f and g are integers from 0 ~ 4 and h and i are  
integers from 0 ~ 6.)]

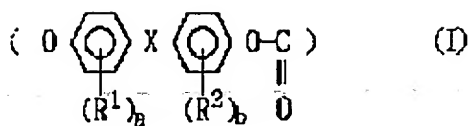
[Scope of patent claims]

[Claim 1]

The electro-photographic photoreceptor consisting of a  
photosensitive layer formed on electro-conductive  
baseboard has the characteristic of using polycarbonate  
possessing the repetitive units shown by the formula (I)

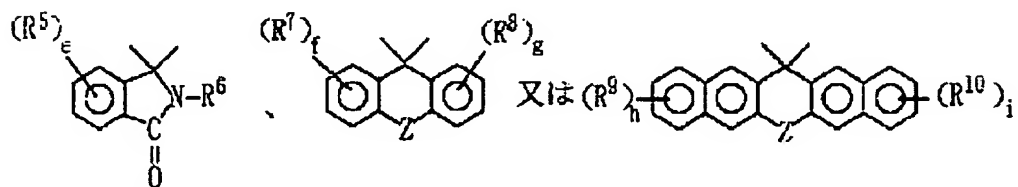
given below,

[Formula 1]



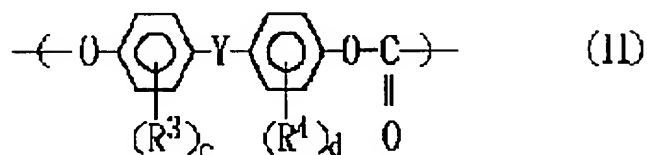
[Wherein,  $\text{R}^1$  and  $\text{R}^2$  independently show halogen atom, alkyl radical having 1 ~ 12 carbon atoms, cyclo hexyl radical, aryl radical or substituted aryl radical having 8 ~ 12 carbon atoms, a and b are integers from 0 ~ 4 and X is the radical shown by the formula given below.

[Formula 2]



(Wherein,  $\text{R}^5$ ,  $\text{R}^7$ ,  $\text{R}^8$ ,  $\text{R}^9$  and  $\text{R}^{10}$  mean the same as  $\text{R}^1$ ,  $\text{R}^6$  shows alkyl radical having 1 ~ 12 carbon atoms, cyclo alkyl radical, aryl or substituted aryl radical having 8 ~ 12 carbon atoms, Z is a single bond, - O -, - CO -, - S -, - SO - or - SO<sub>2</sub> -, e, f and g are integers from 0 ~ 4 and h and i are integers from 0 ~ 6.)] or the polycarbonate

[Formula 3]



[Detailed description of the invention]

[0001]

[Industrial applicability]

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resin in the photosensitive layer. In further details, the present invention relates to the electro-photographic photoreceptor that maintains mechanical strength such as surface hardness and electro-photography property for a long period and that can be used in different electro-photography fields.

[0002]

[Techniques of the past]

Polycarbonate is being used in many fields as basic material, however, development of a material having further excellent properties is demanded for, accompanying the widening of application fields.

[0003]

Recently, 2 types are used in the electro-photographic photoreceptor. The first is the laminate type organic electro-photographic photoreceptor (OPC) in which photosensitive layer possesses at least 2 layers, charge generating layer (CGL) that generates charge by exposure



and charge transporting layer (CTL) that transports charge, and the 2<sup>nd</sup> is single layer type electro-photographic photoreceptor in which photosensitive layer is formed by dispersing charge generating layer and charge transporting layer in the binder resin. In both these types, polycarbonate resin manufactured by using bis phenol A as the raw material is widely used as the binder resin of photosensitive layer of charge transporting layer of laminate type electro-photographic photoreceptor and single layer type electro-photographic photoreceptor.

[0004]

The polycarbonate resin manufactured by using bis phenol A as the raw material has satisfactory compatibility with the charge transporting layer material due to which the photoreceptor possessing photosensitive layer using this as the binder resin, has satisfactory electrical properties and possesses the advantage of having comparatively high mechanical strength.

[0005]

However, in the case of forming photosensitive layer using the polycarbonate resin that is manufactured by using bis phenol A as the binder resin, problems ① and ② given below occur.

① At the time of manufacturing photoreceptor, the coating layer gets whitened (gelled) at the time of coating the photosensitive layer by the used solvent and the photosensitive layer easily gets crystallized. In the part in which this crystallization occurs, the charge remains present as residual potential without getting reduced, which appears as the defect in picture quality.

② In the case of common negative electric charge type electro-photographic photoreceptor, the photosensitive layer formed by using polycarbonate resin that is manufactured by using bis phenol A as the raw material, gets peeled off as its adhesion property with the first coat is deteriorating and moreover, gets scratched as the surface

hardness is insufficient due to which aberration of surface takes place and print resistant life becomes short. Normally, the first coat stated here indicates electro-conductive baseboard in single layer type photoreceptor and opposite layer type photoreceptor and in the case of laminating charge transporting layer and charge transporting layer on the conductor in this order such as positive electric charge electro-photographic photoreceptor, the conductor becomes the first coat. Moreover, in the case of forming blocking layer or intermediate layer between the conductor and charge transporting layer or charge transporting layer and charge generating layer with the aim of improving electro-photography property, this becomes the first coat.

[0006]

[Problems the invention solves]

The present invention has been devised based on the circumstances mentioned above. The present invention aims at solving the problems mentioned above that are observed

in the electro-photographic photoreceptor of the past in which polycarbonate resin manufactured by using bis phenol A as the raw material is used as the binder resin of photosensitive layer, and offering an electro-photographic photoreceptor that has excellent practical use, with no whitening (gelation) of coating liquid taking place at the time of manufacture of electro-photographic photoreceptor, and that maintains excellent mechanical strength such as printing resistance for a long period and has excellent electro-photography property.

[0007]

[Method to solve the problems]

The authors of the present invention carried out an earnest research in order to solve the problems mentioned above as a result of which they showed that electro-photographic photoreceptor prepared by using a polycarbonate having a specific structure as the binder resin of photosensitive layer, maintains excellent mechanical strength for a long

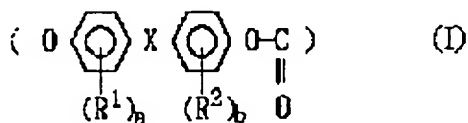
usage period and has excellent electro-photography property without whitening (gelation) of coating liquid taking place at the time of manufacturing photoreceptor, as in case of electro-photographic photoreceptor of the past in which polycarbonate resin manufactured by using bis phenol A as the raw material is used as the binder resin. Based on this knowledge, the present invention was completed.

[0008]

Namely, the present invention offers the electro-photographic photoreceptor consisting of a photosensitive layer formed on electro-conductive baseboard has the characteristic of using polycarbonate possessing the repetitive units shown by the formula (I) given below,

[0009]

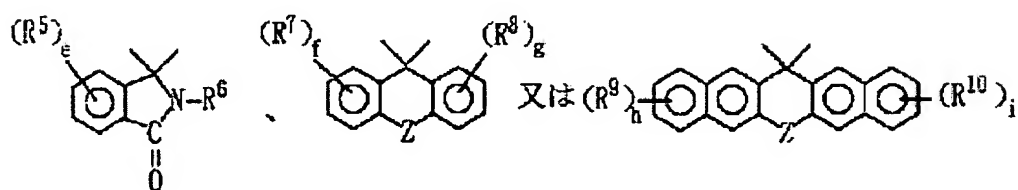
[Formula 4]



[Wherein,  $R^1$  and  $R^2$  independently show halogen atom, alkyl radical having 1 ~ 12 carbon atoms, cyclo hexyl radical, aryl radical or substituted aryl radical having 8 ~ 12 carbon atoms, a and b are integers from 0 ~ 4 and X is the radical shown by the formula given below.

[0010]

[Formula 5]

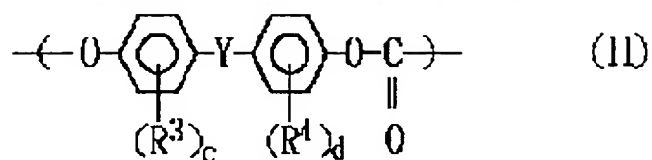


(Wherein,  $R^5$ ,  $R^7$ ,  $R^8$ ,  $R^9$  and  $R^{10}$  mean the same as  $R^1$ ,  $R^6$  shows alkyl radical having 1 ~ 12 carbon atoms, cyclo alkyl radical, aryl or substituted aryl radical having 8 ~ 12 carbon atoms, Z is a single bond, - O -, - CO -, - S -, - SO - or - SO<sub>2</sub> -, e, f and g are integers from 0 ~ 4 and h and i are integers from 0 ~ 6.)) or the polycarbonate formed from the repetitive units shown by the general formula (II) given below, as the binder resin of photosensitive

layer mentioned above.

[0011]

[Formula 6]



[Wherein,  $\text{R}^3$  and  $\text{R}^4$  mean the same as  $\text{R}^1$  and Y shows single bond, - O -, - CO -, - S -, - SO -, - SO<sub>2</sub> -, - CR<sup>11</sup>R<sup>12</sup> - (here,  $\text{R}^{11}$  and  $\text{R}^{12}$  independently show hydrogen atom, tri fluoro methyl radical, alkyl radical having 1 ~ 6 carbon atoms or aryl or substituted aryl radical having 6 ~ 12 carbon atoms.), 1, 1 - cyclo alkylene radical having 5 ~ 8 carbon atoms or  $\alpha$ ,  $\omega$  - alkylene radical having 2 ~ 12 carbon atoms.]

[0012]

Moreover, the polycarbonate used in the present invention can possess repetitive units other than those given above within the range such that aim of the present invention is not lost. Moreover, other polycarbonate component or additive can be blended in appropriate quantity and used.

[0013]

The reduced viscosity  $[\eta_{sp}/c]$  of the polycarbonate used in the present invention, measured over the solution formed by using methylene chloride as the solvent and having concentration of 0.5 g/dl at 20°C is desired to be within the range from 0.2 ~ 2.5 dl/g. If the reduced viscosity  $[\eta_{sp}/c]$  is less than 0.2 dl/g, then mechanical strength of the polycarbonate lowers, particularly, surface hardness of the layer that is formed by using this polycarbonate as the binder resin, lowers due to which aberration of photoreceptor takes place and print resistant life becomes short. On the other hand, if the reduced viscosity  $[\eta_{sp}/c]$  exceeds 2.5 dl/g, then solution viscosity of the polycarbonate increases and manufacture of photoreceptor by solution coating method becomes difficult. The proportion of repetitive units shown by the general formula (I)  $[(I)/(I) + (II)]$ , in terms of molar ratio, should be more than 0.01, desirably, more than 0.05.

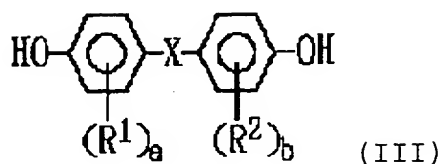


[0014]

The polycarbonate used in the present invention is manufactured by reacting divalent phenol (III) shown by the general formula given below

[0015]

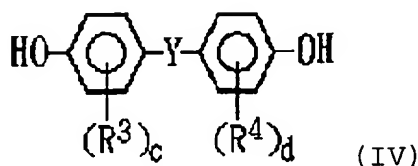
[Formula 7]



(Wherein,  $R^1$ ,  $R^2$ ,  $a$ ,  $b$ ,  $X$ ,  $R^5$ ,  $R^6$ ,  $R^7$ ,  $R^8$ ,  $R^9$ ,  $R^{10}$ ,  $Z$ ,  $e$ ,  $f$ ,  $g$ ,  $h$  and  $i$  mean the same as described above.) or divalent phenol (III) and divalent phenol (IV) shown by the general formula given below

[0016]

[Formula 8]



(Wherein,  $R^3$ ,  $R^4$ ,  $c$ ,  $d$ ,  $Y$ ,  $R^{11}$  and  $R^{12}$  mean the same as described above.) with carbonic acid ester (carbonate)

forming compound.

[0017]

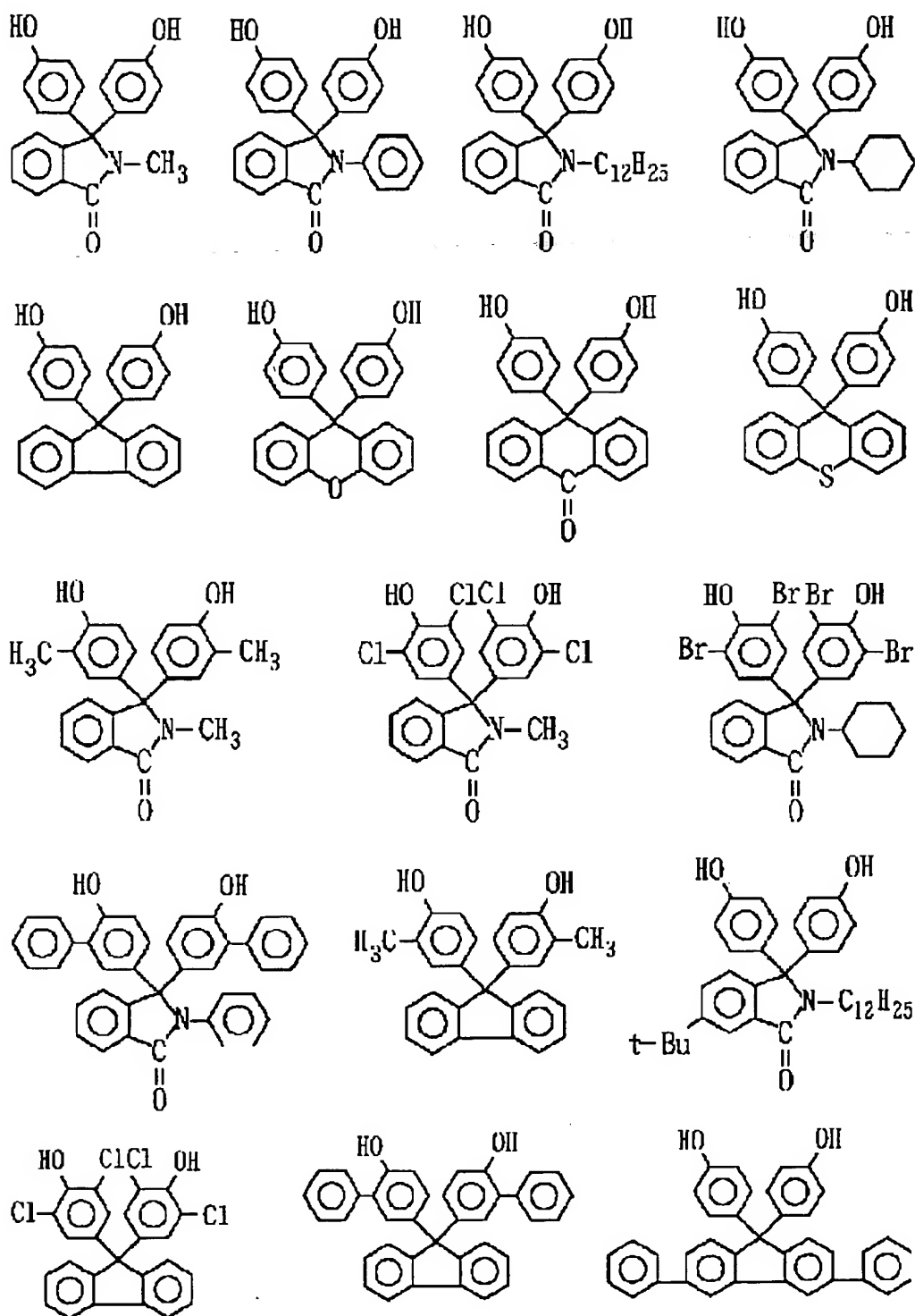
This reaction is carried out either by carrying out polycondensation reaction using different carbonic acid ester (carbonate) forming compounds such as carbonyl dihalides for example, phosgene etc., halo formates such as chloro formate compound etc. or carbonic acid ester (carbonate) compound in the presence of appropriate acid binder, or by carrying out ester exchange (transesterification) reaction using bis aryl carbonate as the ester carbonate forming compound.

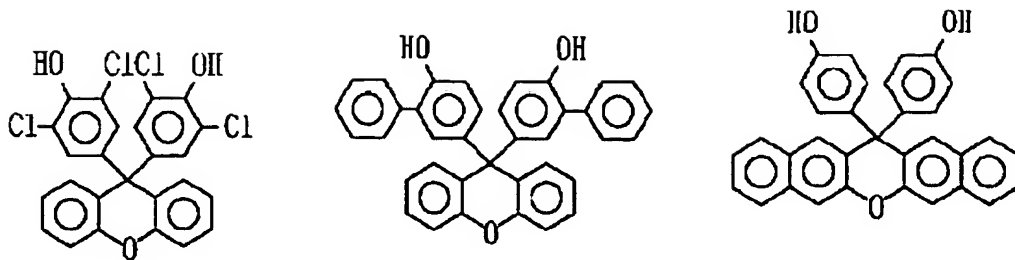
[0018]

As regards the concrete examples of divalent phenol (III) shown by the general formula (III), compounds given below can be used.

[0019]

[Formula 9]





[0020]

Moreover, as regards the concrete examples of divalent phenol (IV) shown by the general formula (IV) given above, bis (4 - hydroxy phenyl) methane, 1, 1 - bis (4 - hydroxy phenyl) ethane, 1, 2 - bis (4 - hydroxy phenyl) ethane, 2, 2 - bis (4 - hydroxy phenyl) propane, 2, 2 - bis (3 - methyl - 4 - hydroxy phenyl) butane, 2, 2 - bis (4 - hydroxy phenyl) butane, 2, 2 - bis (4 - hydroxy phenyl) octane, 4, 4 - bis (4 - hydroxy phenyl) heptane, 3, 3 - bis (4 - hydroxy phenyl) pentane, 4, 4' - di hydroxy tetra phenyl methane, 1, 1 - bis (4 - hydroxy phenyl) - 1 - phenyl ethane, 1, 1 - bis (4 - hydroxy phenyl) - 1 phenyl methane, bis (4 - hydroxyphenyl) ether, bis (4 - hydroxyphenyl) sulfide, bis (4 - hydroxy phenyl) sulfone, 1, 1 - bis (4 - hydroxy phenyl) cyclo pentane, 1, 1 - bis (4 - hydroxy phenyl) cyclo

hexane, 2, 2 - bis (3 - methyl - 4 - hydroxy phenyl) propane,  
 2 - (3 - methyl - 4 - hydroxy phenyl) - 2 - (4 - hydroxy  
 phenyl) - 1 - phenyl ethane, bis (3 - methyl - 4 - hydroxy  
 phenyl) sulfide, bis (3 - methyl - 4 - hydroxyphenyl) sulfone,  
 bis (3 - methyl - 4 - hydroxy phenyl) methane, 1, 1 - bis  
 (3 - methyl - 4 - hydroxy phenyl) cyclo hexane, 2, 2 - bis  
 (2 - methyl - 4 - hydroxy phenyl) propane, 2, 2 - bis (3,  
 6 - di methyl - 4 - hydroxy phenyl) propane, 2, 2 - bis  
 (3 - cyclo hexyl - 4 - hydroxy phenyl) propane, 1, 1 - bis  
 (2 - butyl - 4 - hydroxy - 5 - methyl phenyl) butane, 1,  
 1 - bis (2 - tert - butyl - 4 - hydroxy - 3 - methyl phenyl)  
 ethane, 1, 1 - bis (2 - tert - butyl - 4 - hydroxy - 5 -  
 methyl phenyl) propane, 1, 1 - bis (2 - tert - butyl - 4  
 - hydroxy - 5 - methyl phenyl) butane, 1, 1 - bis (2 - tert  
 - butyl - 4 - hydroxy - 5 - methyl phenyl) iso butane, 1,  
 1 - bis (2 - tert - butyl - 4 - hydroxy - 5 - methyl phenyl)  
 heptane, 1, 1 - bis (2 - tert - butyl - 4 - hydroxy - 5  
 - methyl phenyl) - 1 - phenyl methane, 1, 1 - bis (2 - tert

- amyl - 4 - hydroxy - 5 - methyl phenyl) butane, bis (3  
 - chloro - 4 - hydroxy phenyl) methane, 2, 2 - bis (3 -  
 chloro - 4 - hydroxy phenyl) propane, 2, 2 - bis (3 - fluoro  
 - 4 - hydroxy phenyl) propane, 2, 2 - bis (3 - bromo - 4  
 - hydroxy phenyl) propane, 2, 2 - bis (3, 5 - di fluoro  
 - 4 - hydroxy phenyl) propane, 2, 2 - bis (3, 5 - di chloro  
 - 4 - hydroxy phenyl) propane, 2, 2 - bis (3, 5 - di bromo  
 - 4 - hydroxy phenyl) propane, 2, 2 - bis (3 - bromo - 4  
 - hydroxy - 5 - chloro phenyl) propane, 2, 2 - bis (3, 5  
 di chloro - 4 - hydroxy phenyl) butane, 2, 2 - bis (3, 5  
 di bromo - 4 - hydroxy phenyl) butane, 1 - phenyl - 1, 1  
 - bis (3 - fluoro - 4 - hydroxy phenyl) ethane, bis (3 -  
 fluoro - 4 - hydroxy phenyl) ether, 1, 1 - bis (3 - cyclo  
 hexyl - 4 - hydroxy phenyl) cyclo hexane, 4, 4' - di hydroxy  
 bi phenyl, 4, 4' - di hydroxy - 3, 3' - di methyl bi phenyl,  
 4, 4' - di hydroxy - 2, 2' - di methyl bi phenyl, 4, 4'  
 - di hydroxy - 3, 3' - di cyclo hexyl bi phenyl, 3, 3' -  
 di fluoro - 4, 4' - di hydroxy bi phenyl, 2, 2 - bis (4

- hydroxy phenyl) hexa fluoro propane, 2, 2 - bis ( 3 - phenyl - 4 - hydroxy phenyl) propane, 1, 1 - bis ( 3 - phenyl - 4 - hydroxy phenyl) cyclo hexane, 1, 1 - bis ( 3 - methyl - 4 - hydroxy phenyl) cyclo hexane, bis (4 - hydroxy phenyl) sulfone, bis (3 - phenyl - 4 - hydroxy phenyl) sulfone, bis (4 - hydroxy phenyl) ether etc. can be given. These divalent phenols can be used independently or as a mixture of 2 or more than 2 types.

[0021]

Among these examples also, 2, 2 - bis (4 - hydroxy phenyl) propane, 1, 1 - bis (4 - hydroxy phenyl) cyclo hexane, 4, 4' - di hydroxy tetra phenyl methane, 1, 1 - bis (4 - hydroxy phenyl) - 1 phenyl ethane, bis (4 - hydroxy phenyl) sulfone, 2, 2 - bis (3 - methyl - 4 - hydroxy phenyl) propane, 4, 4' - di hydroxy bi phenyl and 2, 2 - bis (3 - phenyl - 4 - hydroxy phenyl) propane, 2, 2 - bis (4 - hydroxy phenyl) hexa fluoro propane, 1, 1 - bis (4 - hydroxy - 3 - methyl phenyl) cyclo hexane, 3, 3 - bis (4 - hydroxy phenyl) pentane,

2, 2 - bis (4 - hydroxy - 3 - cyclo hexyl phenyl) propane,  
2, 2 - bis (3, 5 - di bromo - 4 - hydroxy phenyl) propane,  
2, 2 - bis (4 - hydroxy - 3, 6 - di methyl phenyl) propane,  
bis (4 - hydroxy phenyl) ether etc. are desired to be used.

[0022]

As regards the carbonic acid ester (carbonate) forming compound mentioned above, carbonyl dihalide mentioned above, halo formates, carbonate compounds etc. can be used and the polycondensation reaction carried out in the presence of acid binder is generally carried out in a solvent.

[0023]

The proportion with which carbonic acid ester (carbonate) forming compound is used, should be appropriately regulated taking into consideration the chemical theoretical ratio (equivalent) of the reaction. Moreover, in the case of using gas form carbonic acid ester (carbonate) forming compound such as phosgene, the method of blowing these into the reaction system is desired to be used.



[0024]

As regards the acid binder mentioned above, alkali metal hydroxides such as sodium hydroxide, potassium hydroxide etc., alkali metal carbonate salt such as sodium carbonate, potassium carbonate etc., organic bases such as pyridine etc. or their mixture is used.

[0025]

The proportion with which acid binder is used also, should be appropriately regulated taking into consideration the chemical theoretical ratio (equivalent) of the reaction as mentioned above. Concretely, acid binder is used with the quantity of 2 equivalent or slight excess quantity with respect to number of moles of the used divalent phenol (generally, 1 mole is equivalent to 2 equivalent).

[0026]

As regards the solvent mentioned above, well-known different solvents used in the manufacture of polycarbonate can be used independently or as mixed solvent. As regards

the representative examples, hydrocarbon solvent such as xylene, halogenated hydrocarbon solvent such as methylene chloride, chloro benzene etc. can be given. Interface polycondensation reaction using 2 types of solvents that do not get mixed can be carried out.

[0027]

Moreover, reaction is desired to be carried out by adding catalyst such as tertiary amine for example, tri ethyl amine or quaternary ammonium salt in order to accelerate the polycondensation reaction. Moreover, oxidation preventing agent such as sodium sulfite, hydro sulfide etc. can be added in small quantity as per requirement. Reaction is carried out at the temperature within the range from 0 ~ 150°C, desirably, 5 ~ 40°C. Reaction pressure can be reduced pressure, normal pressure or elevated pressure, however, reaction can be desirably carried out under normal pressure or the natural pressure of reaction system. Reaction duration differs with reaction temperature, however, generally, it

is within the range from 0.5 minutes ~ 10 hours, desirably,  
1 minute ~ 2 hours.

[0028]

As regards the bis aryl carbonate used in the latter ester exchange (transesterification) reaction of divalent phenol and bis aryl carbonate, di - p - toluyyl carbonate, phenyl - p - toluyyl carbonate, di - p - chloro phenyl carbonate, di naphthyl carbonate etc. can be given. As regards the reaction method of this method, fusion polycondensation method, solid phase polycondensation method can be used. In the case of using fusion polycondensation method, reaction is carried out in the fused state at high temperature under reduced pressure. The reaction is generally carried out at the temperature within the range from 150 ~ 350°C, desirably, 200 ~ 300°C. In the case of using solid phase polycondensation method, polycondensation is carried out by heating in the solid phase state at the temperature below the melting point of the generated polycarbonate. In both the cases, pressure

is reduced desirably below 1 mm Hg in the final stage of reaction and phenols originating in bis aryl carbonate mentioned above generated by ester exchange (transesterification) reaction are removed out of the system. The reaction duration differs with reaction temperature or degree of reduced pressure, however, it is generally within the range from 1 ~ 4 hours. Reaction is desired to be carried out in the atmosphere of inert gas such as nitrogen or argon. Moreover, oxidation preventing agent mentioned above can be added as per requirement.

[0029]

The reduced viscosity  $[\eta_{sp}/c]$  of the obtained polycarbonate can be regulated within the range mentioned above by different methods such as selection of reaction conditions mentioned above or regulation of usage quantity of terminal sealing (end capping) agent mentioned above. Moreover, in some cases, appropriate physical treatments (mixing, division etc.) as well as / or chemical treatments.

(polymer reaction, bridging treatment, partial decomposition treatment etc.) are performed on the obtained polycarbonate to obtain the polycarbonate having the desired reduced viscosity  $[\eta_{sp}/c]$ .

[0030]

The obtained reaction product (crude product) is subjected to different well-known post-treatment such as separation refining etc. and polycarbonate having desired purity (refined) can be recovered.

[0031]

The electro-photographic photoreceptor of the present invention is restricted to use the polycarbonate mentioned above as the binder resin in the single layer type and laminate type photoreceptor and it can be any well-known type of electro-photographic photoreceptor, however, it is desired to be used as the binder resin of charge transporting layer of the laminate type electro-photographic photoreceptor in which photosensitive layer possesses at least 1 charge

generating layer and at least 1 charge transporting layer.

[0032]

In the electro-photographic photoreceptor of the present invention, polycarbonate mentioned above of the present invention can be used independently or as a mixture of 2 or more than 2 types. Moreover, it can also contain binder resin component of other polycarbonate within the range such that a aim of the present invention is not lost. Furthermore, it can also contain additive such as oxidation preventing agent etc.

[0033]

As regards the electro-conductive baseboard material used in the electro-photographic photoreceptor of the present invention, different well-known material can be used, for example, metal plate, drum or metal sheet of aluminium, brass, copper, nickel, steel etc., baseboard formed by vapor depositing electro-conductive material such as aluminium, nickel, chromium, palladium, graphite on a plastic sheet

and performing the treatment of making it electro-conductive such as coating by etc., baseboard formed by performing metal oxide treatment on the surface of metal drum by electrode oxidation, or baseboard formed by performing the treatment of making it electro-conductive on baseboards such as glass, plastic sheet, cloth, paper etc. can be used.

[0034]

The charge generating layer of the laminate type electro-photographic photoreceptor possesses at least 1 charge generating material and this charge generating layer can be formed either by forming a layer of charge generating material on the baseboard by vacuum vapor deposition, sputter method etc., or by forming a layer that is formed by binding the charge generating material using a binder resin on the baseboard. Different well-known methods can be used to form the charge generating layer using binder resin, however, the method in which the coating liquid formed by dispersing or dissolving the charge generating material and binder

resin in an appropriate solvent is coated on the baseboard and then, dried is desired to be used.

[0035]

As regards the charge generating material mentioned above, different well-known materials can be used, for example, selenium material such as non-crystalline selenium, triagonal selenium etc., selenium alloy such as selenium - tellurium etc., selenium compound or selenium-containing composite such as  $\text{As}_2\text{Se}_3$  etc., inorganic material formed from group II and group IV elements such as zinc oxide,  $\text{CdS} - \text{Se}$  etc., oxide type semiconductor such as titanium oxide, different inorganic materials such as silicon group material for example, amorphous silicon, different organic materials such as metallic or non-metallic phthalocyanine, cyanine, anthracene, bis azo compound, pyrene, perilene (?), pirilium salt (?), thia pirilium salt (?), polyvinyl carbazol, squalium pigment etc. can be used.

[0036]



Moreover, these can be used independently or as a mixture of 2 or more than 2 types.

[0037]

There is no particular restriction over binder resin of charge generating layer mentioned above and different well-known resin can be used. As regards the concrete examples, thermoplastic resins such as polystyrene, polyvinyl chloride, polyvinyl acetate, vinyl chloride - vinyl acetate polymer, polyvinyl acetal, alkyd resin, acrylic resin, polyacrylonitrile, polycarbonate, polyamide, polyketone, polyacrylamide, butyral resin, polyester etc., heat-hardening type resins such as polyurethane, epoxy resin, phenol resin etc. can be given.

[0038]

Moreover, as regards the binder resin of charge generating layer mentioned above, polycarbonate mentioned above can be used.

[0039]

Next, charge transporting layer mentioned above can be obtained by forming a layer that is formed by binding charge transporting material by binder resin, on the baseboard.

[0040]

Different well-known methods can be used to form this charge transporting layer using binder resin, however, the method in which the coating liquid formed by dispersing or dissolving the charge transporting material and polycarbonate mentioned above in an appropriate solvent is coated on the baseboard and then, dried is desired to be used.

[0041]

In this charge transporting layer, polycarbonate mentioned above can be used independently or as a mixture of 2 or more than 2 types. Moreover, it can also contain other binder resin component can be used jointly with the polycarbonate of the present invention within the range such that aim of the present invention is not lost.

[0042]

As regards the charge transporting material that can be used in the present invention, electron transporting material and positive hole transporting material used since past can be used.

[0043]

As regards the concrete examples of electron transporting material, electron-absorbing material such as chloranyl, bromanyl, 2, 3 - di chloro - 5, 6 - di cyano - p - benzoquinone, tetra cyano ethylene, tetra cyanoquino di methane, 2, 4, 7 - tri nitro - 9 - fluorenone, 2, 5, 7 - tri nitro - 9 - fluorenone, 2, 4, 7 - tri nitro - 9 - di cyano methylene fluorenone, 2, 4, 5, 7 - tetra nitro xanthone, 2, 4, 9 - tri nitro thio xanthone or di phenoquione derivative such as 3, 5 - di methyl - 3', 5' - di - t - butyl - 4, 4' - di phenoquione etc. or material obtained by polymerizing these electron-absorbing materials can be given. Moreover, these can be used independently or as a mixture of 2 or

more than 2 types.

[0044]

As regards the examples of positive hole transporting material, hydrazones such as pyrene, N - ethyl carbozol, N - iso propyl carbazol, N - methyl - N - phenyl hydrazino - 3 - methyldene - 9 - ethyl carbazol, N, N - di phenyl hydrazino - 3 - methyldene - 9 - ethyl carbazol, N, N - di phenyl hydrazino - 3 - methyldene - 10 - ethyl phenothaizine, N, N - di phenyl hydrazino - 3 - methyldene - 10 - ethyl phenoxadine, p - di ethyl amino benzaldehyde - N, N - di phenyl hydrazone, p - di ethyl amino benzaldehyde - N -  $\alpha$  - naphtyl - N - phenyl hydrazone, p - pyrrolidono benzaldehyde - N, N - di phenyl hydrazone, 1, 3, 3 - tri methyl indolenine -  $\omega$  - aldehyde - N, N - di phenyl hydrazone, p - di ethyl benzaldehyde - 3 - methyl benzothiazolinone - 2 - hydrazone, 1 - phenyl - 1, 2, 3, 4 - tetra hydroquinoline - 6 - carboxy aldehyde - 1', 1' - di phenyl hydrazone etc., pyrazolines such as 2, 5 - bis (p - di ethyl amino phenyl)

- 1, 3, 4 - oxa di azole, 1 - phenyl - 3 - (p - di ethyl  
 amino styril) - 5 - (p - di ethyl amino phenyl) pyrazoline,  
 1 - [quinolyl (2)] - 3 - (p - di ethyl amino styril) - 5  
 - (p - di ethyl amino phenyl) pyrazoline, 1 - [lepidyl (?)  
 (2)] - 3 - (p - di ethyl amino styril) - 5 - (p - di ethyl  
 amino phenyl) pyrazoline, 1 - [6 - methoxy - pyridyl (2)]  
 - 3 - (p - di ethyl amino styril) - 5 - (p - di ethyl amino  
 phenyl) pyrazoline, 1 - [pyridyl (5)] - 3 - (p - di ethyl  
 amino phenyl) pyrazoline, 1 - [pyridyl (2)] - 3 - (p - di  
 ethylaminostyril) - 5 - (p - di ethylaminophenyl) pyrazoline,  
 1 - [pyridyl (2)] - 3 - (p - di ethyl amino styril) - 4  
 - methyl - 5 - (p - di ethyl amino phenyl) pyrazoline, 1  
 - [pyridyl (2)] - 3 - ( $\alpha$  - methyl - p - di ethyl amino styril)  
 - 5 - (p - di ethyl amino phenyl) pyrazoline, 1 - phenyl  
 - 3 - (p - di ethyl amino styril) - 4 - methyl - 5 - (p  
 - di ethyl amino phenyl) pyrazoline, 1 - phenyl - 3 - ( $\alpha$   
 - benzyl - p - di ethyl amino styril) - 5 - (p - di ethyl  
 amino phenyl) pyrazoline, spiro pyrazolone etc., oxazol

group compounds such as 2 - (p - di ethyl amino styril) - 8 - di ethyl amino benzoxazol, 2 - (p - di ethyl amino styril) - 4 - (p - di ethyl amino phenyl) - 5 - (2 - chloro phenyl) oxazol etc., thiazol group compounds such as 2 - (p - di ethyl amino styril) - 6 - di ethyl amino benzo thiazol etc., tri aryl methane group compounds such as bis (4 - di ethyl amino - 2 - methyl phenyl) - phenyl methane etc., poly aryl amines such as 1, 1 - bis (4 - N, N - di ethyl amino - 2 - methyl phenyl) heptane, 1, 1, 2, 2 - tetra quis (4 - N, N - di methyl amino - 2 - methyl phenyl) ethane etc., benzidine group compounds such as N, N' - di phenyl - N, N' - bis (methyl phenyl) benzidine, N, N' - di phenyl - N, N' - bis (ethyl phenyl) benzidine, N, N' - di phenyl - N, N' - bis (propyl phenyl) benzidine, N, N' - di phenyl - N, N' - bis (butyl phenyl) benzidine, N, N' - di phenyl - N, N' - bis (iso propyl phenyl) benzidine, N, N' - di phenyl - N, N' - bis (t - butyl phenyl) benzidine, N, N' - di phenyl - N, N' - bis (t - butyl phenyl) benzidine,

N, N' - di phenyl - N, N' - bis (chloro phenyl) benzidine etc. or butadiene group compounds, tri phenyl amine, poly -N-vinyl carbazole, polyvinyl pyrene, polyvinyl anthracene, organic polysilane, pyrene - formaldehyde resin, ethyl carbazole - formaldehyde resin etc. can be given.

[0045]

Moreover, these can be used independently or as a mixture of 2 or more than 2 types.

[0046]

As regards the concrete examples of solvent mentioned above used at the time of formation of charge generating layer and charge transporting layer mentioned above, aromatic solvents such as benzene, toluene, xylene, chloro benzene etc., ketones such as acetone, methyl ethyl ketone, cyclo hexanone etc., alcohols such as methanol, ethanol, iso propanol etc., esters such as ethyl acetate, ethyl cellosolve etc., halogenated hydrocarbon such as carbon tetrachloride, chloroform, dichloromethane, tetrachloro

ethane etc., ethers such as tetra hydro furan, dioxane etc., dimethyl formamide, dimethyl sulfoxide, diethyl formamide etc. can be given.

[0047]

These solvents can be used independently or as a mixture of 2 or more than 2 types.

[0048]

Coating of each layer can be carried out by using well-known coating device such as applicator, spray coater, bar coater, chip coater, roll coater, dip coater, doctor blade etc.

[0049]

The photosensitive layer of single layer type electro-photographic photoreceptor contains at least charge generating material and charge transporting material mentioned above in the polycarbonate mentioned above that is used as binder resin and different well-known methods can be used to form this photosensitive layer, however, the method in which coating liquid formed by dispersing



or dissolving charge generating material, charge transporting material and binder resin in an appropriate solvent, is coated on the baseboard and then dried, is desired to be used.

[0050]

Moreover, other binder resin can be used jointly with the polycarbonate of the present invention within the range such that aim of the present invention is not lost.

[0051]

The electro-photographic photoreceptor of the present invention has excellent practical use, with no whitening (gelation) of coating liquid taking place at the time of manufacture of electro-photographic photoreceptor, and it maintains excellent mechanical strength such as printing resistance for a long period and has excellent electro-photography property, and therefore, it can be used in different electro-photography fields.

[0052]

[Practical examples]

The present invention has been explained below in further details with the help of practical examples and comparative examples. However, the present invention is not restricted only to these practical examples and it can be changed subject to the condition that gist of the present invention is not deviated.

[0053]

The present invention has been explained below in further details with the help of practical examples. However, the present invention is not restricted only to these practical examples.

[0054]

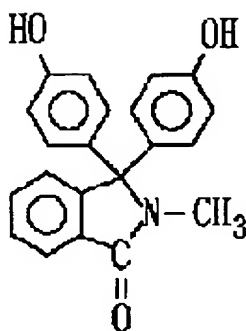
Practical example 1

42.6 g (0.205 mol) of 2, 2 - bis (4 - hydroxy phenyl) propane and 15.4 g (0.051 mol) of di hydroxy aryl compound given below taken as raw material monomers, 550 ml of 8 % aqueous solution of sodium hydroxide, 400 ml of methylene

chloride, 0.15 g of p - tert - butanol taken as terminal sealing (end capping) agent (molecular weight controlling agent) and 3 ml of 10 % aqueous solution of tri ethyl amine taken as catalyst, were taken in a reactor attached with a barrier plate and polycondensation reaction was carried out by blowing phosgene gas simultaneously while maintaining the temperature of reaction liquid in the vicinity of 10°C and stirring it vigorously.

[0055]

[Formula 10]

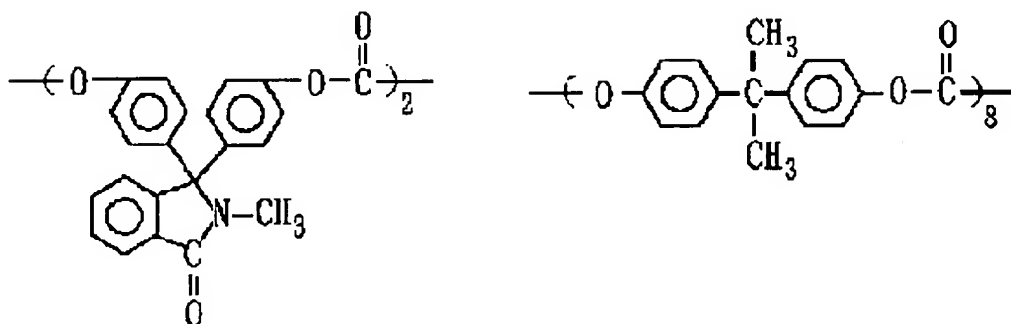


After the completion of reaction, organic layer was diluted by adding 1 liter of methylene chloride and it was washed with water, dilute hydrochloric acid and water in this order after which it was poured into methanol when

polycarbonate polymer was obtained. The reduced viscosity  $[\eta_{sp}/c]$  of the polymer thus obtained, measured over the solution formed by using methylene chloride as the solvent and having concentration of 0.5 g/dl at 20°C was 0.78 dl/g. It was confirmed from  $^1\text{H}$  - NMR spectrum analysis that it is formed from the repetitive units given below.

[0056]

[Formula 11]



Tetra hydro furan solution containing 50 weight % of hydrazone compound given below was prepared as charge transporting material. This coating liquid was kept undisturbed for 1 month, however no whitening and gelation was observed. Next, aluminium was used as electro-conductive baseboard and this coating liquid was coated on charge

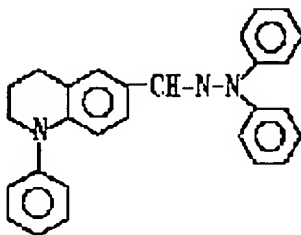
generating layer having thickness of approximately  $0.5\text{ }\mu\text{m}$  formed from oxotitaniumphthalocyanine by dip coating method and then dried after which charge transporting layer having thickness of  $20\text{ }\mu\text{m}$  was formed and thus, laminated type electro-photographic photoreceptor was prepared. At the time of coating, charge transporting layer did not undergo crystallization. Moreover, electro-photography property was measured by using static electric charge test device EPA - 8100 (Kawaguchi Denki Seisakujo (Kawaguchi Electrical Works) make). Corona discharge of  $-6\text{ KV}$  was carried out and initial surface potential ( $V_0$ ), residual potential ( $V_R$ ) after irradiation ( $10\text{ Lux}$ ) and half reduced exposure quantity ( $E_{1/2}$ ) were measured. The results have been presented in table 1 given below. Moreover, anti - aberration property of this charge transporting layer was evaluated by using aberration testing device. Experiment conditions: sample was subjected to reciprocating motion for 1200 times on aberration paper attached with the load of  $200\text{ g}$  and change

in the reduced aberration quantity after that was measured.

The results have been presented in table 2 given below.

[0057]

[Formula 12]



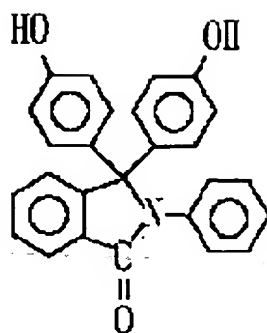
[0058]

Practical example 2

54.9 g (0.205 mol) of 1, 1 - bis (4 - hydroxy phenyl) cyclohexane and 20.0 g (0.051 mol) of dihydroxyaryl compound given below taken as monomers were used. Other than this change, procedure similar to practical example 1 was carried out and polymer having repetitive units given below ( $[\eta_{sp}/c]$  = 0.81 dl/g) was obtained.

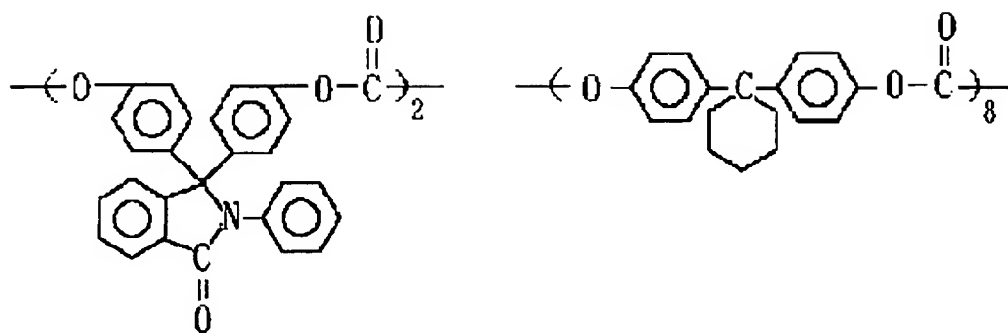
[0059]

[Formula 13]



[0060]

[Formula 14]



This polymer was used and laminate type electro-photographic photoreceptor was prepared by the procedure similar to practical example 1. Results of evaluation of stability of coating liquid and crystallization at the time of coating were similar to that of practical example 1. Moreover, results of evaluation of electro-photography property and anti aberration property have been presented in table 1 and 2 respectively.

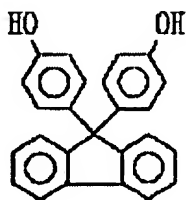
[0061]

Practical example 3

72.2 g (0.205 mol) of 4, 4' - di hydroxy tetra phenyl methane and 20.0 g (0.051 mol) of di hydroxy aryl compound given below taken as monomers were used. Other than this change, procedure similar to practical example 1 was carried out and polymer having repetitive units given below ( $[\eta_{sp}/c]$  = 0.82 dl/g) was obtained.

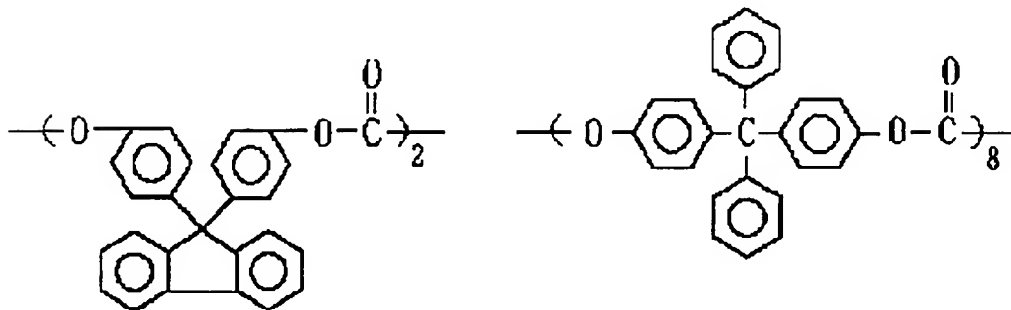
[0062]

[Formula 15]



[0063]

[Formula 16]





This polymer was used and laminate type electro-photographic photoreceptor was prepared by the procedure similar to practical example 1. Results of evaluation of stability of coating liquid and crystallization at the time of coating were similar to that of practical example 1. Moreover, results of evaluation of electro-photography property and anti aberration property have been presented in table 1 and 2 respectively.

[0064]

#### Comparative example 1

Polycarbonate obtained by using the marketed polymer, 1, 1 - bis (4 - hydroxy phenyl) propane (terminal sealing (end capping) agent p - tert butyl phenol) ( $[\eta_{sp}/c] = 0.76$  dl/g) was used and laminate type electro-photographic photoreceptor was prepared by the procedure similar to practical example 1. As a result, coating liquid got whitened on the 3<sup>rd</sup> day and gelation also took place. Moreover, a part of charge transporting layer got crystallized

(whitened) at the time of coating. Moreover, results of evaluation of electro-photography property and anti aberration property have been presented in table 1 and 2 respectively.

[0065]

#### Comparative example 2

Polycarbonate obtained by using the marketed polymer, 1, 1-bis (4 - hydroxyphenyl) cyclohexane (terminal sealing (end capping) agent p - tert butyl phenol) ( $[\eta_{sp}/c] = 0.78$  dl/g) was used and laminate type electro-photographic photoreceptor was prepared by the procedure similar to practical example 1. As a result, coating liquid got whitened on the 2<sup>nd</sup> day and gelation also took place. Moreover, a part of charge transporting layer got crystallized (whitened) at the time of coating. Moreover, results of evaluation of electro-photography property and anti aberration property have been presented in table 1 and 2 respectively.

[0066]

[Table 1]

Electro-photography property

	Initial surface potential $V_0$ (V)	Residual potential $V_R$ (V)	Half reduced exposure quantity $E_{1/2}$ (Lux·sec)
Practical example 1	- 750	- 1	0.78
" 2	- 742	- 2	0.80
" 3	- 768	- 2	0.70
Comparative example 1	- 752	- 3	0.84
" 2	- 752	- 3	0.81

[0067]

[Table 2]

Anti aberration property

	Aberration quantity (mg)
Practical example 1	1.70

" 2	1.66
" 3	1.68
Comparative example 1	2.36
" 2	1.86

[0068]

[Effect / result of the invention]

If the present invention is used, then polycarbonate possessing a specific structure is used as the binder resin of photosensitive layer of the electro-photographic photoreceptor due to which coating liquid does not get whitened (gelled) at the time of preparing electro-photographic photoreceptor and therefore, life of electro-photographic photoreceptor can be increased and surface hardness of photoreceptor surface, namely, anti aberration property can be improved and electro-photographic photoreceptor having excellent printing resistance in which electro-photography property has been maintained even after long repetitive use, can

be offered.

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Continued from front page

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